Magnetic Fluctuations in a Charge-Ordered State of the One-Dimensional Extended Hubbard Model with a Half-Filled Band

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Magnetic properties in a charge-ordered state are examined for the extended Hubbard model at half-filling. Magnetic excitations, magnetic susceptibilities and a nuclear spin relaxation rate are calculated with taking account of fluctuations around the mean-field solution. The relevance of the present results to the observation in the 1:1 organic conductors, (TTM-TTP)I_3, is discussed.

KEYWORDS: extended Hubbard model, half-filling, (TTM-TTP)I_3, charge order, magnetism

Organic conductors are one of the most suitable materials for studying exotic electronic correlation effects in low dimensional systems. Quasi one-dimensional (1-D) quarter-filled conductors, Bechgaard salts $(TMTSF)_2X$ and their sulfur analog $(TMTTF)_2X$, have been intensively studied and it has been found that the rich phases, *e.g.*, spin-Peierls states, spin density wave (SDW) state, superconductivity and so on, are realized as a function of temperature, T, and (effective) pressure.[1)]

Recently, the 1:1 organic material, (TTM-TTP)I_3, has been synthesized[2)] and studied experimentally.[3,4,5,6,7)] By extended Hückel molecular orbital calculation, the transfer integral along the stacking direction is estimated as $t_c = 0.26$eV and is much larger than the others, t_a, t_b <0.01eV.[4)] Therefore, the electronic structure is highly 1-D along the stacking axis. Different from $(TMTSF)_2X$ and $(TMTTF)_2X$, the compound has a half-filled band. Although a 1-D electron system at half-filling is in the Mott insulating state, the material shows metallic conduction for higher temperature and exhibits metal-insulator (MI) transition at $T_c = 120$-160 K.[4,5)] Below this temperature region, the gap in the spin excitation has been observed in measurement of magnetic susceptibility[5,6,7)] and nuclear spin relaxation rate.[7)] In addition, X-ray measurements[5,6)] and NMR spectrum[7)] indicate the appearance of the charge order below T_c. Thus, the MI transition of this material is followed by the charge order and the spin gap, and is different from the transition in the quasi 1-D quarter-filled organic materials.

Since nearest-neighbor repulsion plays a crucial role for the charge order, the 1-D extended Hubbard model (EHM) with on-site, U, and nearest-neighbor repulsion, V, is considered to be appropriate for studying the above properties. The ground state of 1-D EHM at half-filling has been investigated theoretically.[8,9,10,11,12,13,14,15)] Recent investigations by numerical[16,17)] and analytical calculations[18)] have shown the phase diagram on the plane of U and V as follows. In the case of large U and V, the SDW state is dominant for $U \gtrsim 2V$, whereas for $U \lesssim 2V$ the charge density wave (CDW) state corresponding to the charge order is realized where the charge-rich and poor sites appear alternatively. The transition between the two kinds of density waves is the first order. In the case of small U and V, in addition to the two kinds of density waves, the bond charge density wave (BCDW) state appears in the narrow region between the SDW and CDW states. The transition from BCDW to SDW or CDW is continuous. We note that the phase diagram closely resembles that by mean-field theory[9)] where the first order transition occurs at $U = 2V$ and the SDW (CDW) state is realized for $U > 2V$ ($U < 2V$). To the best of our knowledge, however, the properties for finite temperature corresponding to observation in (TTM-TTP)I_3 and excitation spectra have not been investigated.

In the present paper, magnetic properties of the charge-ordered state in the 1-D EHM at half-filling are examined based on the mean-field treatment. Since the mean-field theory reproduces the phase diagram very well except the BCDW state, and the interchain coupling exists in the real materials, the treatment based on the mean-field solution seems to be appropriate for describing the properties in (TTM-TTP)I_3 except the weak interaction region with $U \simeq 2V$. Gaussian fluctuations around the mean-field solution are taken into account by using the path integral method. The magnetic excitation spectra, magnetic susceptibilities and a nuclear spin relaxation rate are investigated.

We consider the 1-D EHM given by the following Hamiltonian, $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\rm int}$, where

$$\mathcal{H}_0 = -t \sum_{j,s} \left(c^\dagger_{j,s} c_{j+1,s} + \text{h.c.} \right) = \sum_{k,s} \epsilon_k c^\dagger_{k,s} c_{k,s}, \quad (1)$$

$$\begin{aligned} \mathcal{H}_{\rm int} &= \frac{U}{2} \sum_{j,s} n_{j,s} n_{j,-s} + V \sum_{j,s,s'} n_{j,s} n_{j+1,s'} \\ &= \sum_{-Q_0 < q \le Q_0} \Big\{ \Big(\frac{U}{4N} + \frac{V}{N} \cos qa \Big) n(q) n(-q) \\ &\qquad - \frac{U}{4N} m(q) m(-q) \Big\}. \end{aligned} \quad (2)$$

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Here, t is the transfer energy between the nearest-neighbor site, $\epsilon_k = -2t\cos ka$ with lattice constant a, and $Q_0 = \pi/a$. The quantity, $c^\dagger_{j,s}(= 1/\sqrt{N}\sum_k \mathrm{e}^{-\mathrm{i}kx_j}c^\dagger_{k,s})$, denotes the creation operator of the electron at the j-th site with spin s, $n(q) = \sum_{j,s}\mathrm{e}^{\mathrm{i}qx_j}c^\dagger_{j,s}c_{j,s}$, $m(q) = \sum_{j,s}\mathrm{e}^{\mathrm{i}qx_j}sc^\dagger_{j,s}c_{j,s}$, and N is the number of lattices (and electrons). We express the action corresponding to the above Hamiltonian by Grassmann algebras and decompose the interaction parts into bilinear forms by utilizing the Stratonovich-Hubbard transformation. The resulting action is written as,

$$\mathcal{S} = \int_0^\beta \mathrm{d}\tau\Big\{\sum_{k,s} c^*_{k,s}(\tau)(\partial_\tau - \mu + \epsilon_k)c_{k,s}(\tau) + \sum_{-Q_0<q\le Q_0}\Big[-(\frac{U}{4N}+\frac{V}{N}\cos qa)\rho(q,\tau)\rho(-q,\tau) + (\frac{U}{2N}+\frac{2V}{N}\cos qa)\rho(q,\tau)n(-q,\tau) + \frac{U}{4N}\sigma(q,\tau)\sigma(-q,\tau) - \frac{U}{2N}\sigma(q,\tau)m(-q,\tau)\Big]\Big\}, \quad (3)$$

where $\beta = 1/T$ and μ is the chemical potential. Here, we express $\nu(0,\tau) = \nu_0 + \delta\nu(0,\tau)$, $\nu(Q_0,\tau) = \nu_{Q_0} + \delta\nu(Q_0,\tau)$ and $\nu(q,\tau) = \delta\nu(q,\tau)$ with $0 < |q| < Q_0$ ($\nu = \rho$ or σ), and expand $\mathcal{S}$ up to the second order of $\delta\nu$. Then the electron degrees of freedom are integrated out. The mean-field equations determining ν_0 and ν_{Q_0} are obtained under the condition where the average of the terms including the first order fluctuation vanish. In case of $U < 2V$, the charge-ordered state, where $\sigma_0 = \sigma_{Q_0} = 0$, becomes most stable, and the energy gap $\Delta = (U/2 - 2V)\rho_{Q_0}/N$ is determined by

$$\Delta = \frac{2V - U/2}{N}\sum_k \frac{\Delta}{E_k}\left\{f(-E_k) - f(E_k)\right\}, \quad (4)$$

with $f(x) = 1/(\mathrm{e}^{\beta x}+1)$ and $E_k = \sqrt{\epsilon_k^2 + \Delta^2}$. The chemical potential is given by $\mu = (U/2+2V)\rho_0/N$ with $\rho_0 = N$.

The effective action up to the second order is obtained as $\mathcal{S}_{\mathrm{eff}} = \sum_{\nu=\rho,\sigma}\mathcal{S}^\nu_{\mathrm{eff}}$, where $\mathcal{S}^\nu_{\mathrm{eff}} = \sum_{\omega_n,-Q_0<q\le Q_0} A^\nu(q,\mathrm{i}\omega_n)\delta\nu(-q,-\mathrm{i}\omega_n)\delta\nu(q,\mathrm{i}\omega_n)$. The quantity, $A^\nu(q,\mathrm{i}\omega_n)$, is given as follows,

$$A^\rho(q,\mathrm{i}\omega_n) = -(\frac{U}{4N}+\frac{V}{N}\cos qa) \times\left\{1-(\frac{U}{N}+\frac{4V}{N}\cos qa)K(q,\mathrm{i}\omega_n)\right\}, \quad (5)$$

$$A^\sigma(q,\mathrm{i}\omega_n) = \frac{U}{4N}\left\{1+\frac{U}{N}K(q,\mathrm{i}\omega_n)\right\}, \quad (6)$$

where

$$K(q,\mathrm{i}\omega_n) = \sum_{-Q_0<k\le Q_0}\sum_{\alpha=\pm,\gamma=\pm}\frac{1}{4} \times(\frac{f(E_k)-f(\alpha E_{k+q})}{E_k - \alpha E_{k+q} + \mathrm{i}\gamma\omega_n})(1+\alpha\frac{\epsilon_k\epsilon_{k+q}+\Delta^2}{E_kE_{k+q}}). \quad (7)$$

It should be noted that there is no coupling between the fluctuation with the wavenumber q and that with $q-Q_0$ although the lattice periodicity changes to $2a$ due to formation of the charge order. The reason for the absence of the above coupling will be discussed below.

Charge and spin susceptibilities, $\chi_\rho(q,\mathrm{i}\omega_n)$ and $\chi_\sigma(q,\mathrm{i}\omega_n)$, and the local susceptibilities, $\chi_\nu(x_i,x_i;\mathrm{i}\omega_n)$, are given as follows,

$$\chi_\rho(q,\mathrm{i}\omega_n) = \frac{1}{N}\Big\{\langle\delta\rho(q,\mathrm{i}\omega_n)\delta\rho(-q,-\mathrm{i}\omega_n)\rangle + \frac{2N}{U+4V\cos qa}\Big\}, \quad (8)$$

$$\chi_\sigma(q,\mathrm{i}\omega_n) = \frac{1}{N}\left\{\langle\delta\sigma(q,\mathrm{i}\omega_n)\delta\sigma(-q,-\mathrm{i}\omega_n)\rangle - \frac{2N}{U}\right\}, \quad (9)$$

$$\chi_\nu(x_i,x_i;\mathrm{i}\omega_n) = \frac{1}{N}\sum_q \chi_\nu(q,\mathrm{i}\omega_n), \quad (10)$$

where

$$\langle\delta\nu(q,\mathrm{i}\omega_n)\delta\nu(-q,-\mathrm{i}\omega_n)\rangle = \frac{1}{2A^\nu(q,\mathrm{i}\omega_n)}. \quad (11)$$

We note that the spatially alternating component of the local susceptibilities, which is written as $(-1)^i/N^2\sum_q\langle\delta\nu(q,\mathrm{i}\omega_n)\delta\nu(-q+Q_0,-\mathrm{i}\omega_n)\rangle$, vanishes due to $\langle\delta\nu(q,\mathrm{i}\omega_n)\delta\nu(-q+Q_0,-\mathrm{i}\omega_n)\rangle = 0$, *i.e.*, the absence of coupling between the fluctuation with q and that with $q-Q_0$. Thus, the local susceptibilities in the charge-rich site are the same as those in the poor site. It is understood in terms of the particle-hole (p-h) transformation as follows. The Hamiltonian, eqs.(1) and (2), are invariant under the p-h transformation, $c_{j,\sigma} \to (-1)^j c^\dagger_{j,\sigma}$. On the other hand, the amount of charge in the charge-rich site changes into that in the poor site and *vice versa* by the p-h transformation. Thus, the p-h transformation exchanges the charge-rich site for the poor site. Therefore, the local quantities at the charge-rich site are equal to those at the poor site. In the following, we discuss the spin degree of freedom in detail.

At first, we investigate the spin excitation spectra, which are given by the solutions of $\chi_\sigma(q,\omega)^{-1} = 0$. We show $\omega(q)$ at $T = 0$ for $U/t = 3.0$ and $V/t = 2.0$ in Fig.1 where the solid curve represents the collective mode and the dotted curves, $\omega_{\mathrm{c}}^{\mathrm{min}}$ and $\omega_{\mathrm{c}}^{\mathrm{max}}$, express the minimum and maximum values of the continuum spectra, respectively. The collective mode appears just below $\omega_{\mathrm{c}}^{\mathrm{min}}$ and has the maximum value for $q = q_{\mathrm{m}} \gtrsim \pi/(2a)$. In addition, the collective mode goes into the continuum spectra at $q \gtrsim 0$ and $q > q_{\mathrm{m}}$. The locations where the mode touches the continuum spectra are indicated by the arrows in Fig.1.

Next we discuss the magnetic susceptibility and nuclear spin relaxation rate, T_1^{-1}, given by $(T_1T)_i^{-1} \propto \lim_{\omega\to 0}\mathrm{Im}\chi_\sigma(x_i,x_i;\omega)/\omega$. As was discussed above, both the local spin susceptibility and $(T_1T)_i^{-1}$ are independent of the site. These results indicate that the split of NMR spectra is not a Knite shift but due to the other origin such as a chemical shift, and the nuclear spins in crystallographically equivalent atoms decay with one kind of relaxation time. Note that it is not obvious whether the same conclusions are obtained or not for the charge-ordered states coexisting with SDW found in

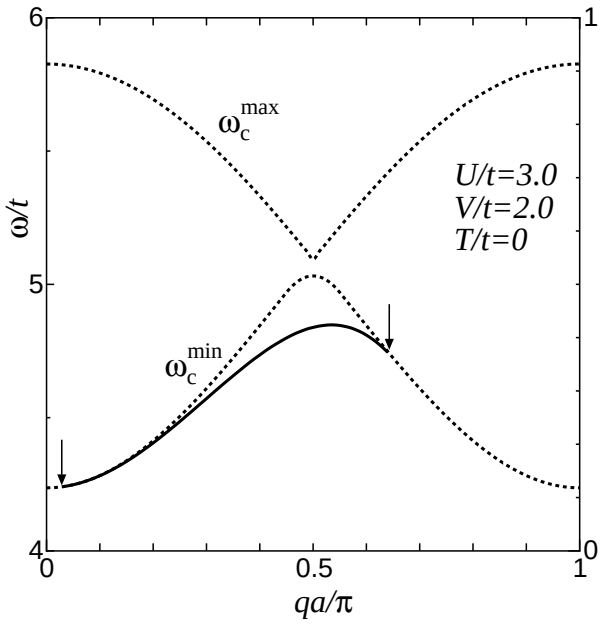

Fig. 1. The spin excitation spectra, ω, as a function of q at $T/t = 0$ in the case of $U/t = 3.0$ and $V/t = 2.0$. Here the solid curve represents the collective mode and the dotted curves, $\omega_c^{\rm min}$ and $\omega_c^{\rm max}$, express the minimum and maximum value of the continuum spectra, respectively. The arrows indicate the locations where the collective mode touches the continuum spectra.

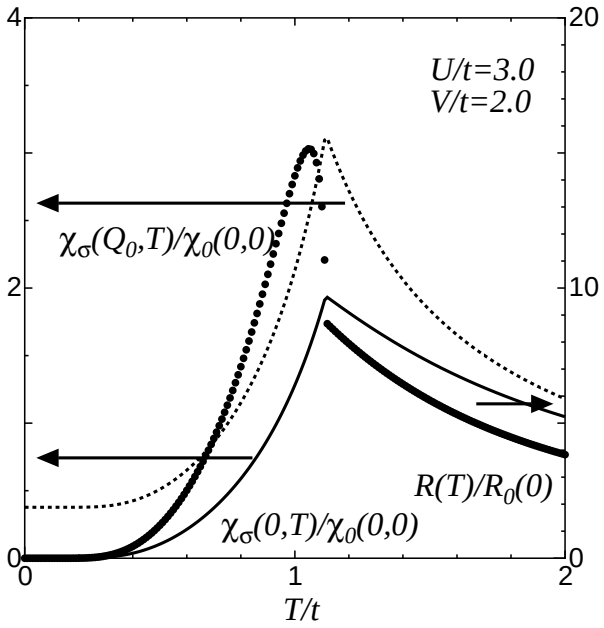

Fig. 2. The magnetic susceptibilities, $\chi_\sigma(0,T)$ and $\chi_\sigma(Q_0,T)$, normalized by $\chi_0(0,0)$ and $R(T) \equiv (T_1T)^{-1}$ normalized by $R_0(0)$ as a function of T in the case of $U/t = 3.0$ and $V/t = 2.0$. Here $\chi_0(0,0)$ and $R_0(0)$ are respectively the susceptibility at $q = 0$ and $T = 0$ and $(T_1T)^{-1}$ at $T = 0$ in the absence of the interaction.

quasi 1-D quarter-filling organic conductors.[19,20] This is because the p-h transformation does not exchange the amount of charge or spin in the rich site for that in the poor site though the Hamiltonian is invariant under the transformation. We show the uniform susceptibility, $\chi_\sigma(0,T)$, the staggered susceptibility, $\chi_\sigma(Q_0,T)$, and $R(T) \equiv (T_1T)^{-1}$ as a function of T in Fig.2. Here $\chi_0(0,0)$ and $R_0(0)$ are the susceptibility and $(T_1T)^{-1}$ at $T = 0$ in the absence of interaction. For $T > T_c$ with T_c being the critical temperature of the CDW, these quantities increase with decreasing temperature. Since T_c is of the order of Fermi energy, $2t$, Curie-like behavior in $\chi_\sigma(0,T)$ is observed. On the other hand, below T_c, the susceptibilities decrease rapidly. The quantity, $R(T)$, is enhanced just below T_c and shows a rapid decrease for $T \ll T_c$. The behavior is the same as Hebel-Schlichter peak in s-wave superconductivity.[21] We note that both quantities, $\chi_\sigma(Q_0,T)$ and $R(T)$, tend to infinity at $T = T_c$ for $U = 2V$, *i.e.*, the boundary between the CDW and the SDW states because the transition between the two density waves is the first order.

Here we consider the magnitude of the interactions. From the reflectance spectra, the on-site interaction, U, and the hopping integral, t, are estimated as $U \simeq 0.57$eV and $t \simeq 0.16$eV at 100K[3] where the nearest-neighbor repulsion is neglected. Since there is a possibility that the magnitude of interaction estimated by the optical measurement is too big for discussing the thermodynamic properties,[22] we may expect smaller values of interactions. In fact, as is shown in Fig.3, when we use $U/t = 0.8$ and $V/t = 0.6$, the transition temperature is close to that for (TTM-TTP)I_3 and the magnetic susceptibility for $T \gtrsim T_c$ does not show Curie-like behavior as was observed in the experiments. In addition, the above choice leads to the resistivity independent of T for high temperature, which is observed in the experiments,[4,5] because the resistivity at half-filling above the charge gap behaves as $T^{4K_\rho-3}$,[23] and $K_\rho = \sqrt{\{1 - V/(2\pi t)\} / \{1 + (U + 5V)/(2\pi t)\}} \simeq 3/4$ in this case (see inset of Fig.3). The magnitude of the interactions we have pointed out are in the weak coupling regime where the BCDW state appears for $U \simeq 2V$. However, the estimation is considered to be sensible as long as the values of the interactions do not belong to the BCDW region in the phase diagram determined numerically[16] and analytically.[18] In fact, the values, $U/t = 0.8$ and $V/t = 0.6$, are in the CDW region of the phase diagram.

In conclusion, we investigated the magnetic properties of 1-D EHM at half-filling with taking account of fluctuation around the mean-field solution. The magnetic excitation spectra at $T = 0$, temperature dependence of the magnetic susceptibilities and that of the nuclear spin relaxation rate are discussed. The local magnetic susceptibility and the nuclear spin relaxation rate are found to be independent of the site even in the charge-ordered state. In addition, we pointed out the possibility that the magnitude of the interaction of the 1:1 material, (TTM-TTP)I_3, is small compared to that estimated from the reflectance spectra.

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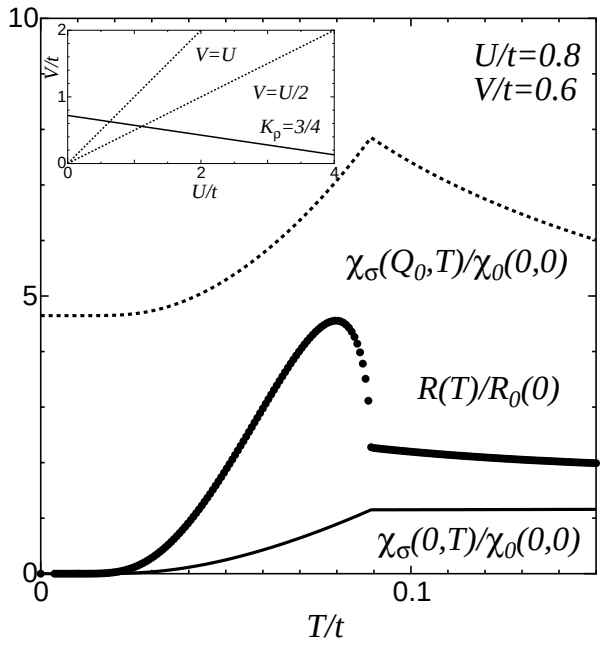

Fig. 3. The magnetic susceptibilities, $\chi_\sigma(0,T)$ and $\chi_\sigma(Q_0,T)$, normalized by $\chi_0(0,0)$ and $R(T) \equiv (T_1T)^{-1}$ normalized by $R_0(0)$ as a function of T in the case of $U/t = 0.8$ and $V/t = 0.6$. Inset : the curve expressing $K_\rho = 3/4$ (solid curve) on the plane of U/t and V/t, where the upper (lower) dotted line expresses $V = U$ ($V = U/2$).

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[1] For review, see, T. Ishiguro, K. Yamaji and G. Saito: Organic Superconductors (Springer-Verlag, Berlin, 1998).
[2] T. Mori, H. Inokuchi, Y. Misaki, T. Yamabe, H. Mori and S. Tanaka: Bull. Chem. Soc. Jpn. **67** (1994) 661.
[3] H. Tajima, M. Arifuku, T. Ohta, T. Mori, Y. Misaki, T. Yamabe H. Mori and S. Tanaka: Synth. Met. **71** (1995) 1951.
[4] T. Mori, T. Kawamoto, J. Yamaura, T. Enoki, Y. Misaki, T. Yamabe, H. Mori and S. Tanaka: Phys. Rev. Lett. **79** (1997) 1702.
[5] M. Maesato, Y. Sasou, S. Kagoshima, T. Mori, T. Kawamoto, Y. Misaki and T. Yamabe: Synth. Met. **103** (1999) 2109.
[6] N. Fujimura, A. Namba, T. Kambe, Y. Nogami, K. Oshima, T. Mori, T. Kawamoto, Y. Misaki and T. Yamabe: Synth. Met. **103** (1999) 2111.
[7] M. Onuki, K. Hiraki, T. Takahashi, D. Jinbo, T. Kawamoto, T. Mori, K. Tanaka and Y. Misaki: J. Phys. Chem. Solids **62** (2001) 405.
[8] R. A. Bari: Phys. Rev. B **3** (1971) 2662.
[9] D. Cabib and E. Callen: Phys. Rev. B **12** (1975) 5249.
[10] J. E. Hirsch: Phys. Rev. Lett. **53** (1984) 2327.
[11] J.W. Cannon and E. Fradkin: Phys. Rev. B **41** (1990) 9435.
[12] J.W. Cannon, R.T. Scalettar and E. Fradkin: Phys. Rev. B **44** (1991) 5995.
[13] J. Voit: Phys. Rev. B **45** (1992) 4027.
[14] P.G.J.van Dongen: Phys. Rev. B **49** (1994) 7904.
[15] G. P. Zhang: Phys. Rev. B **56** (1997) 9189.
[16] M. Nakamura: J. Phys. Soc. Jpn. **68** (1999) 3123, Phys. Rev. B **61** (2000) 16377.
[17] P. Sengupta, A.W. Sandvik and D.K. Campbell: Phys. Rev. B **65** (2002) 155113.
[18] M. Tsuchiizu and A. Furusaki: Phys. Rev. Lett. **88** (2002) 056402.
[19] J.P. Pouget and S. Ravy: J. Phys. I (France) **6** (1996) 1501, Synth. Met. **85** (1997) 1532.
[20] K. Hiraki and K. Kanoda: Phys. Rev. Lett. **80** (1998) 4737.
[21] The enhancement of $(T_1T)^{-1}$ just below T_c in the CDW state is discussed in the following text, G. Grüner: *Density Waves in Solids*, Sec.3 (Addison-Wesley, New York, 1994).
[22] see P.102 in ref. 1.
[23] T. Giamarchi: Phys. Rev. B **44** (1991) 2905.